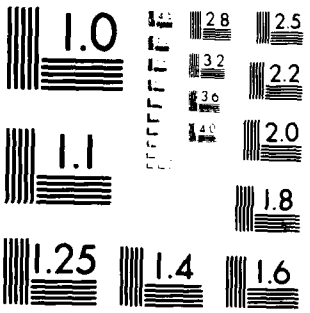
AD-A144 980 DIBLOCK COPOLYMERS OF POLYSTYRENE/12 POLYBUTADIENE AND 1/1
POLYSTYRENE/POLYBU..(U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMICAL ENGINEE.. R E COHEN ET AL.
UNCLASSIFIED 15 AUG 84 TR-13 N00014-77-C-0311 F/G 11/9 NL

END
DATE FILMED
10 84
DTIC



(12)

OFFICE OF NAVAL RESEARCH
Contract N00014-77-C-0311
Task No. NR 356-646

TECHNICAL REPORT NO. 13

Diblock Copolymers of Polystyrene/1,2 Polybutadiene and Polystyrene/ Polybutene-1: Molecular Structure, Morphology and Mechanical Properties

by

R.E. Cohen and J.M. Torradas
MIT Department of Chemical Engineering
Cambridge, MA 02139

August 15, 1984

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Diblock Copolymers of Polystyrene/1,2 Polybutadiene and Polystyrene/Polybutene-1: Molecular Structure, Morphology and Mechanical Properties		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER 13
7. AUTHOR(s) R.E. Cohen and J.M. Torradas		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0311
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR - 356 - 646
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St., Arlington, VA 22217		12. REPORT DATE August 15, 1984
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release and sale; distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

block copolymers
dynamic mechanical properties
hydrogenated elastomers
mechanical behavior

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A novel set of diblock copolymers has been examined in various molecular and morphological characterization experiments, in small amplitude dynamic mechanical tests and in large deformation experiments. In all of the materials studied, one of the block sequences is atactic polystryrene; the second block is comprised of either 1,2 polybutadiene (essentially 100% vinyl ~~adduct and atactic microstructure~~) or its hydrogenated product, polybutene-1 (also atactic). There is a pronounced influence of the hydrogenation of the rubbery phase on the morphology and the properies of the diblock copolymers. Some, but not all, of the changes in

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601 |

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

properties can be accounted for by the 23 C lowering of T_g imparted by the hydrogenation step.

INTRODUCTION

Numerous publications have dealt with the class of materials obtained from block copolymerization of styrene and butadiene.(1) Of these, the majority have been concerned with polybutadiene microstructures which contain predominantly 1,4 adduct (e.g. 45% cis 1,4; 45% trans 1,4; 10% 1,2) which is obtained from butyllithium initiated anionic polymerization in a non-polar hydrocarbon solvent. A few papers have discussed block copolymers and homopolymers containing "high vinyl" polybutadiene (ca. 65% 1,2) obtained when a polar solvent such as THF is employed in the type of polymerization described above. In a few cases the hydrogenated products of these polystryrene/polybutadiene (SB or SBS) block copolymers have been examined. The hydrogenation step leaves the polystyrene moiety unchanged but transforms the polybutadiene block into a saturated hydrocarbon polymer which may be a semicrystalline thermoplastic or an amorphous rubber depending on the original polydiene microstructure.

Of particular interest in regard to the copolymers examined here is the atactic 1,2 microstructure of the polybutadiene moieties, which upon hydrogenation leads to an amorphous rubbery polybutene-1 material. This novel set of materials has enabled us to examine the influence of hydrogenation on morphology and properties while keeping all other essential features of the composite block copolymer materials unchanged. Specifically, by investigating the morphological and mechanical features of certain "parent-child" pairs (prior to and following hydrogenation) we have the possibility of documenting the role of a very small molecular-level perturbation on these macroscopic properties.

EXPERIMENTAL MATERIALS

Two diblock copolymers of polystyrene and 1,2 polybutadiene (PS/1,2B) were prepared for our use by A. Halasa according to previously reported anionic polymerization methods using the polar modifier dipiperidene ethane (2,3). Characterization of the diene microstructure by infrared and NMR methods indicated that essentially pure (99%) 1,2 polybutadiene polymers were obtained as expected (4,5), and this is borne out in the data presented below.

Hydrogenation of the PS/1,2B copolymers to yield polystyrene/polybutene-1 materials (PS/PB-1) was carried out by Halasa using the following procedures which are described in greater detail elsewhere (5,6). Soluble nickle octanoate reduced with tri-isobutyl aluminum was used as a hydrogenation catalyst. The catalyst concentration was around 1 mg per hundred grams of polymer. Hydrogenations were carried out at 48°C in toluene. Infrared and proton NMR experiments indicated that about 95% of the pendant vinyl groups were saturated by these means (5). Osmometry and size exclusion chromatography revealed that essentially no change in degree of polymerization resulted from the hydrogenation procedure.

Two homopolymers of 1,2B were also prepared and hydrogenated by the same procedures. The PB-1 homopolymers, and the PB-1 blocks of the hydrogenated copolymers, are also atactic amorphous materials as revealed by thermal analyses reported earlier (5) and in the data presented here. Table 1 summarizes the molecular characterization data for all of the polymers and copolymers.

SAMPLE PREPARATION

The as-received polymers were dissolved in benzene or toluene without stirring, and then reprecipitated with methanol. An anti-oxidant (Anti-

Table 1 - Polymer Characterization

Sample	Code	Molecular Weight(kg/mol) of: Polystyrene	1,2 Polybutadiene	Polybutene-1	M_w/M_n
PS/1,2B	I	14	85	--	1.09
PS/1,2B	II	12	109	--	1.11
PS/PB-1	I'	14	--	88	--
PS/PB-1	II'	12	--	113	--
1,2B	III	--	29	--	1.06
1,2B	IV	--	85	--	1.08
PB-1	III'	--	--	31	1.06
PB-1	IV'	--	--	88	1.08

Table 2 - Solubility Parameters

Polymer (a)	δ $(cal/cm^3)^{1/2}$	Solvent (b)	δ
Polystyrene	9.05	n-heptane	7.4
1,2 polybutadiene (1,2B)	8.25	cyclohexane	8.2
polybutene-1 (PB-1)	8.05	toluene	8.9
		tetrahydrofuran	9.1
		benzene	9.1
		chloroform	9.3
		methyl ethyl ketone	9.3

(a) Calculated using Hoy's group contribution method (7) as described in Reference (8).

(b) Taken from table in Reference (3)

Ox 330, Ethyl Corporation, Baton Rouge, LA) was added to each solution in the amount of 0.5 wt. % of unsaturated rubber. The precipitated polymers were finally dried in a vacuum oven at 50°C for 2 days and kept in a freezer until further use.

Films of the different polymers (0.3-0.5 mm thickness) were cast from various solvents (Table 2) for use in all the experiments reported here. Starting solutions were prepared at 5 weight %. Stirring was kept to a minimum. A spin casting technique (9) was used to carry out the solvent evaporation at various temperatures. In this method, the 5% polymer solution (50-200 ml) is poured into a temperature controlled, nitrogen-blanketed casting cup which rotates at 3450rpm. Periods of up to 48 hours were used for the production of the films made by this technique.

MECHANICAL TESTING METHODS

Stress-strain measurements were carried out on an Instron Model 1122 Tensile Tester at 298K and at 273K. Crosshead speeds varied from 10 to 1000 mm/min. Test specimens of dimensions about 50 mm length and 5 mm width were cut from the cast sheets using a steel microtome knife mounted in the chuck of a drill press. All curves shown are averaged over at least three runs; repeatability was excellent except for the failure points which reflect the presence of surface flaws. No attempt was made to obtain statistically valid failure data. Cyclic experiments designed to examine

hysteresis were carred out by allowing the sample to rest for 15 minutes at zero load before initiating the second cycle.

Dynamic mechanical measurements were performed at 3.5Hz on a Rheovibron DDV-II-C Viscoelastometer. Temperatures from 230K to 393K were covered in these experiments. Considerations of the required changes in specimen geometry, and the correction factors required to obtain valid measurements on these rubbery polymers, are presented in great detail elsewhere (5,10).

MORPHOLOGY EXAMINATION

Because of the saturated nature of the polybutene-1 moieties, it was not possible to use conventional osmium tetroxide staining for transmission electron microscopic examination of the bulk morphology of our samples. Instead a series of small-angle X-ray scattering (SAXS) experiments were carried out on selected samples. Ni-filtered CuKα radiation from a rotating X-ray generator was the X-ray source. The intensity was measured with a linear position sensitive detector collected in a multi-channel analyzer and transferred to a computer where various corrections and data reduction schemes were applied. Details can be found elsewhere (5).

THERMAL ANALYSIS

Differential scanning calorimetry experiments were performed on a Perkin Elmer DSC-II instrument. Specimens were cooled to the starting temperature at a rate of about 320°C/min and then heated to the maximum temperature of the experiment using a rate of 10°C/min. Glass transition temperatures quoted in the text were taken as the midpoint of the temperature range required to complete the baseline shift.

RESULTS AND DISCUSSION

As mentioned above, the 'parent-child' copolymer pairs I,I' and II,II' indicated in Table 1 represent an unusual opportunity to examine the influence of a small perturbation in molecular structure in various larger scale phenomena, e.g. bulk morphology, thermal transitions, or mechanical behavior. We begin with considerations of the bulk morphology.

Based on Helfand's theory of microphase separation in block copolymers, it should be possible to anticipate the effect of the hydrogenation step on the morphologies of these block copolymers mainly through the polymer-polymer interaction parameter, α. Degree of polymerization does not change as a result of hydrogenation, and estimates of the other relevant parameter, the Kuhn structural length (11), show little effect of the hydrogenation of 1,2B to PB-1. To the extent that α can be estimated (5) adequately from solubility parameters, δ, the problem reduces to establishing the influence of hydrogenation on δ. Table 2 lists estimates of solubility parameters for the polymers of interest here along with those of the various solvents employed in the sample preparation. Values of δ for the polymers, calculated using group contribution (7,8) methods, are sensitive to the value of density used. Densities of 1.05, 0.96 and 0.89 g/cm^3 for PS, 1,2B and PB-1 respectively were used (5) to obtain the values of δ shown in the table, which rank in a meaningful way in terms of repeat unit chemical structure.

Using these solubility parameters to estimate α values it was then straightforward to use the Helfand theory to: (i) determine the expected phase form of the equilibrium morphology for each copolymer and (ii) to calculate the characteristic dimensions of this morphology. The results of these calculations (5) are summarized in Table 3. Several things emerge from these results. First, the driving force for phase separation increases following

Table 3 Morphology Calculations for T=345K

Sample Code	F/NkT (11) for Polystyrene Domain		Radius Å of Polystyrene Domain		Interdomain Distance Å	
	Spheres	Cylinders	Spheres	Cylinders	Spheres	Cylinders
I	-15.93	-16.05	150	108	474	584
I'	-30.69	-30.70	149	100	552	562
II	-13.59	-13.63	136	93	553	597
II'	-26.77	-26.69	134	89	562	592

hydrogenation. Second, these samples lie very near the polystyrene composition which dictates the line of demarkation between spherical PS domains and cylindrical PS domains, i.e. F/NkT values are very similar in columns 2 and 3 of Table 3. However, hydrogenation of the continuous rubbery phase has, according to the theory, the tendency to push the morphology toward spheres of PS in the rubbery continuum. This is particularly true for the higher molecular weight pair II - II'. Third, hydrogenation of the rubbery phase has essentially no influence on the expected polystyrene domain dimensions and plays only a small role in the interdomain distance.

In an attempt to check the trends suggested by the above-mentioned calculations, morphologies of selected samples were examined via SAXS experiments. Five samples, listed in Table 4, were subjected to SAXS analysis and although a limited amount of quantitative information could be obtained from the spectra, certain qualitative information was obtained. First, by assuming a spherical morphology and a cubic lattice, observed domain dimensions were in reasonable agreement with theory for the cyclohexane-cast samples. The spectra for the two toluene-cast samples could only be rationalized meaningfully by assuming a hexagonally packed cylindrical morphology (5). Smaller-than-expected spherical domain sizes have been obtained in previous investigations on block copolymers (12,13); transformation from the spherical to cylindrical morphology when a less selective solvent is employed is another result which has been observed in previous studies (14). Thus the overall assignments of morphology from interpreting SAXS data are consistent with expectations from theory and with the known role of the solvent used in the sample preparation step. These assignments of morphology will be useful later particularly for assistance in interpreting results of large deformation experiments.

Table 4 Results of SAXS Experiments on Selected Samples

Sample Code	Casting Conditions: Solvent	Temperature	Polystyrene Domain: Type[a]	Radius[b]	Interdomain Spacing[c]
I	cyclohexane	298K	spheres[a]	110Å	403Å
I'	cyclohexane	298K	spheres[a]	130Å	470Å
I'	cyclohexane	345K	spheres[a]	114Å	410Å

(a) Assumed [5] on the basis of the results of Table 3 and the selectivity of cyclohexane for the continuous rubbery phase of these materials.

(b) Obtained from the fits of the appropriate single particle form factor to the data[5].

(c) Calculated using domain radii and sample composition assuming a simple cubic lattice for the spheres

Turning to the influence of hydrogenation on properties, it is readily seen in the results of DSC experiments (Figure 1) and dynamic mechanical tests (Figure 2) that the principal change is a significant lowering of the Tg of the rubbery phase following hydrogenation. There are, however, certain other subtleties in these results which warrant attention.

In the DSC experiments (Figure 1) it is apparant that the lower temperature glass transition characteristic of the rubbery phases of the various block copolymers is essentially identical in shape and location to the transition of the corresponding rubbery homopolymer or of the rubbery phase of a corresponding (PS/rubber) homopolymer blend. The polystyrene transitions of the block copolymers are shifted to significantly lower temperatures compared to the PS homopolymer or the PS phase of a blend. Several other groups (14-17) have noted this same phenomenon, with significant segmental mixing at and near the PS domain interface being the the common explanation for the Tg depression. This is a plausible explanation for the observations seen here. This Tg depression of the polystyrene domains does have considerable significance since it is around this range of temperature that the useful elastomeric properties of the diblocks are lost.

This latter point is seen most clearly in the results of dynamic mechanical tests. In Figure 2 it is clear that broad rubbery plateaus are seen for all of the diblocks -- behavior which is much more characteristic of triblock copolymers. In fact, sample I' (PS/PB-1;14/88) cast from toluene exhibits a rubbery plateau which extends more than 75 °C beyond the Tg of the rubbery phase. This tendency of a PS/PB-1 diblock copolymer to level out into an extended rubbery plateau is enhanced somewhat when the molecular weight of the PB-1 phase is increased (Figure 3). The PS/1,2B diblocks also show the rubbery plateau in Figure 2 and, significantly, lose this rubbery behavior at

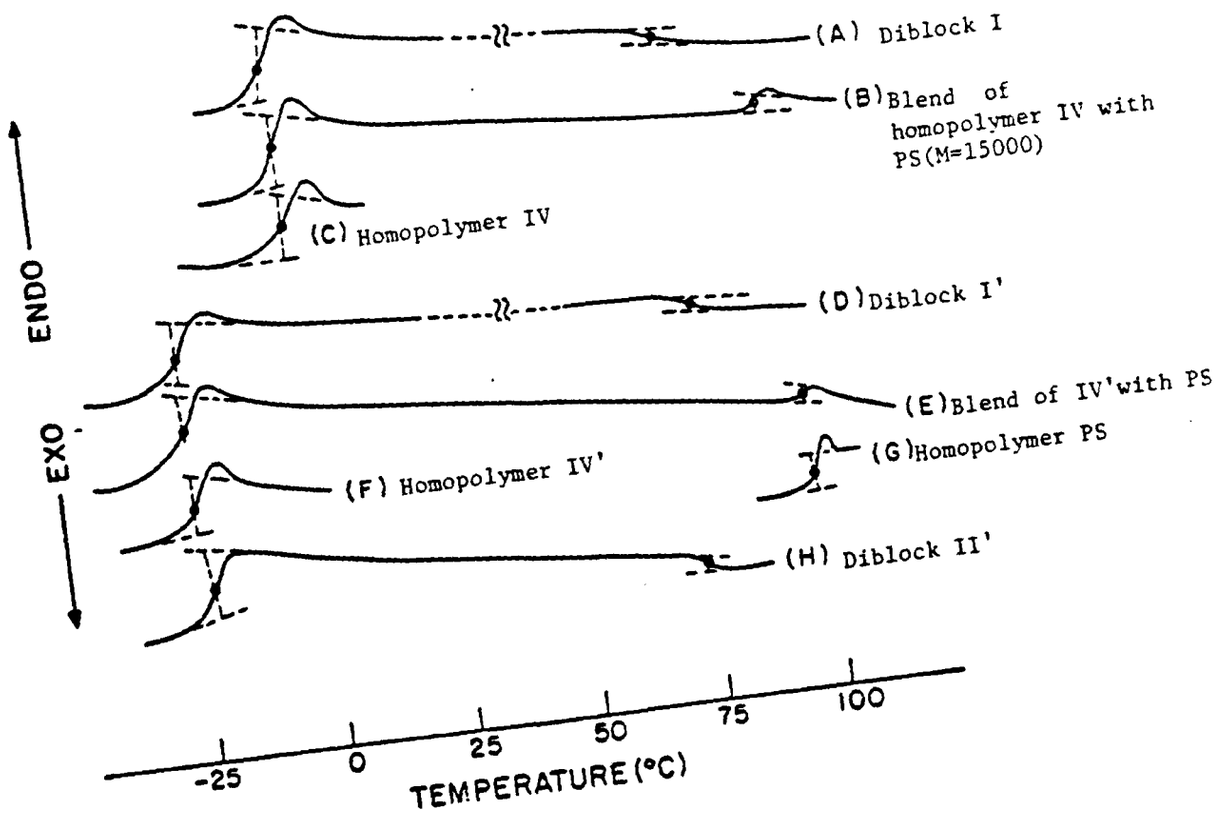
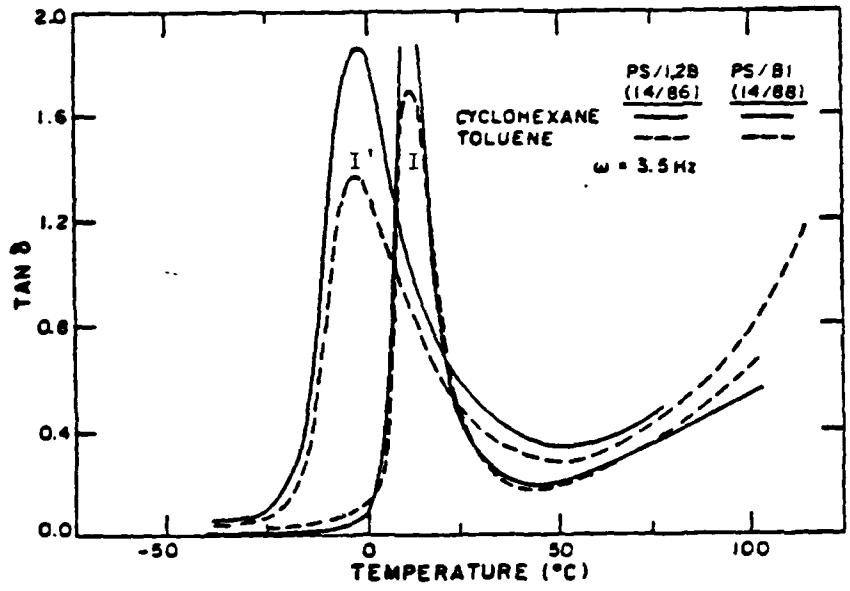

(A) Diblock I
(B) Blend of homopolymer IV with PS(M=15000)
(C) Homopolymer IV
(D) Diblock I'
(E) Blend of IV'with PS
(F) Homopolymer IV'
(G) Homopolymer PS
(H) Diblock II'
ENDO
EXO
-25
0
25
50
75
100
TEMPERATURE (°C)

Figure 1


2.0
1.6
1.2
0.8
0.4
0.0
TAN δ
-50
0
50
100
TEMPERATURE (°C)
PS/1,2B (14/86)
PS/BI (14/88)
CYCLOHEXANE
TOLUENE
ω = 3.5 Hz
I'
I

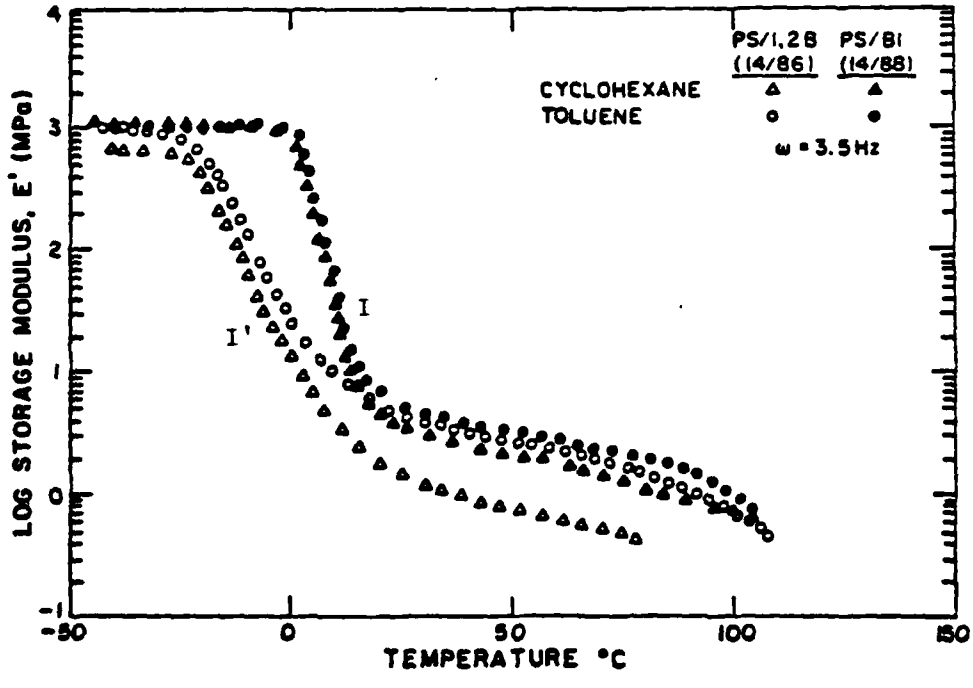

LOG STORAGE MODULUS, E' (MPa)
4
3
2
1
0
-1
-50
0
50
100
150
TEMPERATURE °C
PS/1,2B (14/86)
PS/BI (14/88)
CYCLOHEXANE
TOLUENE
ω = 3.5 Hz
I'
I

Figure 2

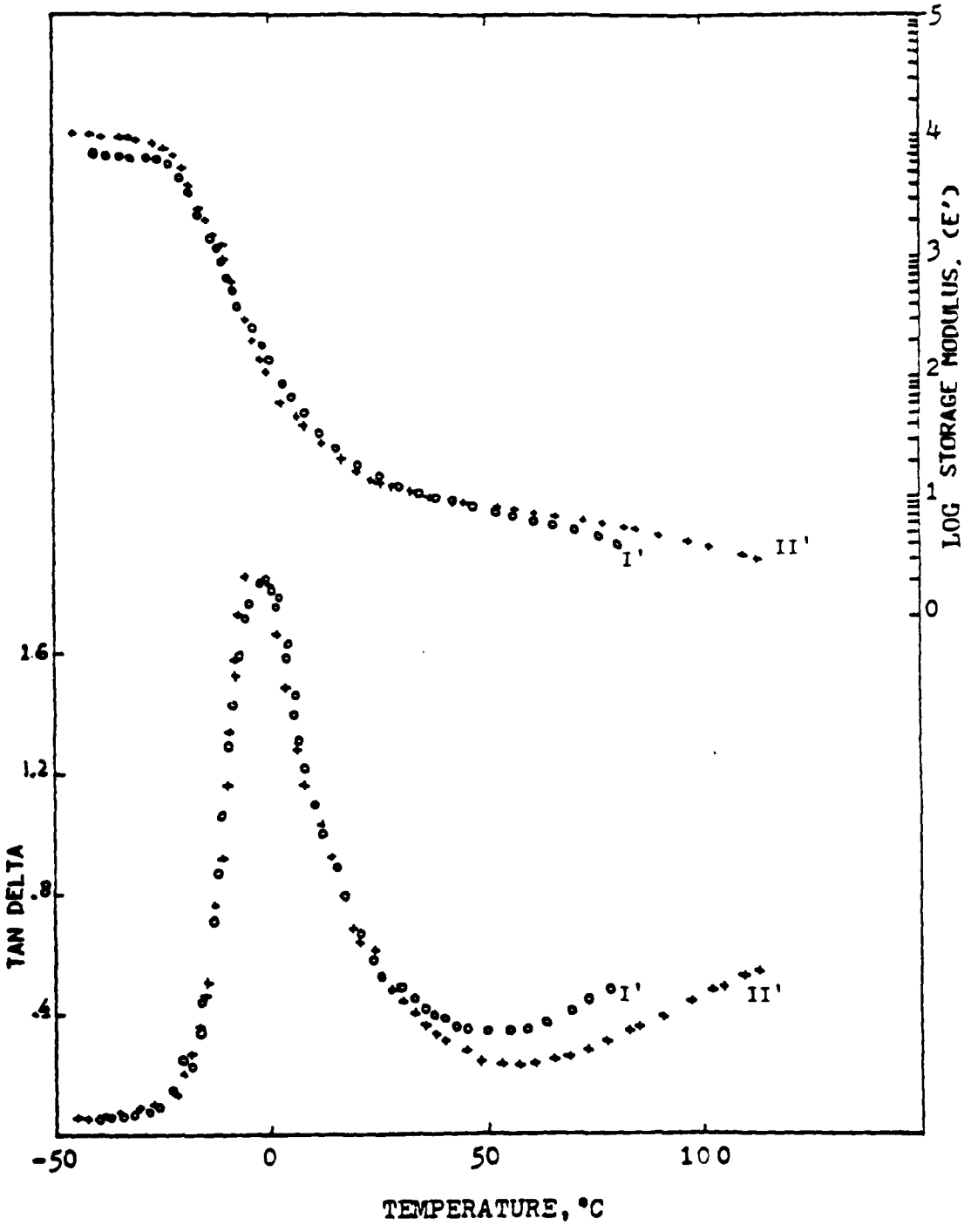
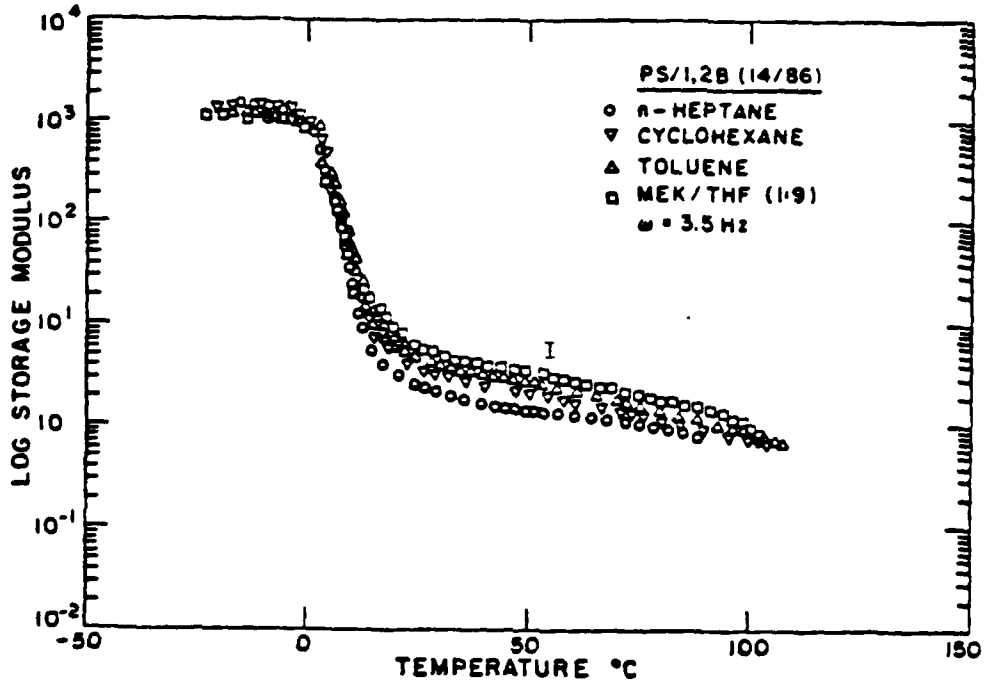

LOG STORAGE MODULUS, (E')
5
4
3
2
1
0
I'
II'
TAN DELTA
1.6
1.2
.8
.4
I'
II'
-50
0
50
100
TEMPERATURE, °C

Figure 3

about the same temperature as the hydrogenated diblocks even though there is about a 25°C difference in the rubbery phase Tg's. Thus, softening of the polystyrene domains is apparantly necessary for these diblocks to lose their energy-storage capabilities. For comparison, we note that earlier work (18) on block copolymers of polystyrene and 1,4 polybutadiene revealed that PS/1,4B diblocks exhibited flow behavior at temperatures very far below the onset of softening of the PS domains, whereas the PS/1,4B/PS triblocks showed rubbery plateaus similar to the present set of diblocks.

There are several possible explanations for the unusual dynamic mechanical behavior of the PS/1,2B and PS/PB-1 diblocks. At the molecular level, the two-carbon side groups could be enhancing inter-chain interactions in the rubbery phases of these materials. However, this same effect should lead to rubbery plateau behavior in the rubbery homopolymers and in rubbery-continuous homopolymer blends with PS. None of these materials exhibited the extended rubbery behavior seen in the diblock and in fact were fluid-like, sticky and impossible to handle without making crosslinked samples. An alternative explanation for the observed results might lie in the possibility that some of the rubbery chains are finding their way back into the PS domain from which they emanate or into neighboring domains, thereby forming permanent loops and bridges which disconnect only as the polystyrene domains begin to soften. A third possibility is that there may be poor phase separation in these samples, so that a thoroughgoing, reticular, polystyrene-rich structure exists in the diblocks. Both of these latter explanations may be examined further by examining more closely the influence of solvent on the (Figure 4) dynamic mechanical properties; furthermore, large deformation mechanical experiments should be particularly revealing in terms of the last hypothesis since a reticular structure should be easily broken during the first stretching of a specimen leading to large hysteresis effects in the stress-STRAIN RESULTS.


PS/1,2B (14/86)
n-HEPTANE
CYCLOHEXANE
TOLUENE
MEK/THF (1:9)
ω = 3.5 Hz
I
LOG STORAGE MODULUS
TEMPERATURE °C

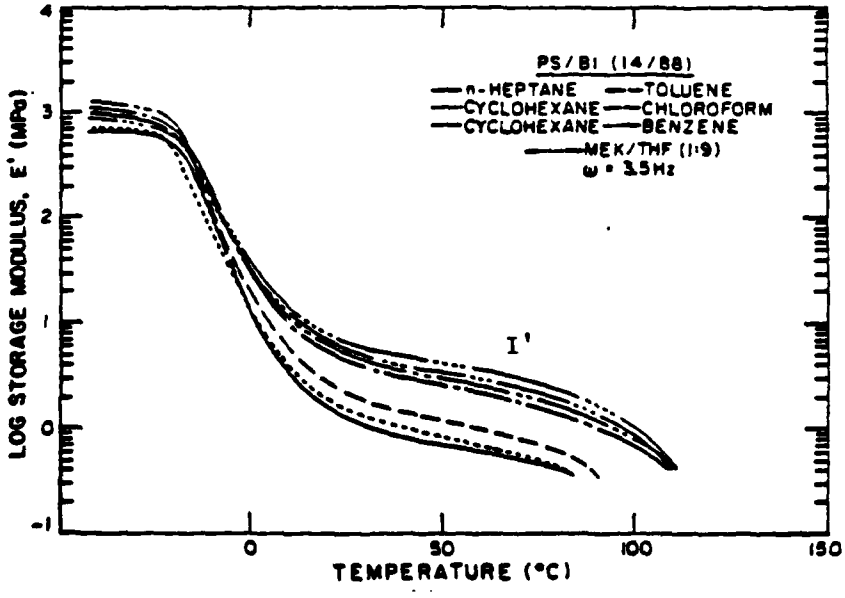

PS/B1 (14/88)
n-HEPTANE
CYCLOHEXANE
CYCLOHEXANE
TOLUENE
CHLOROFORM
BENZENE
MEK/THF (1:9)
ω = 3.5Hz
I'
LOG STORAGE MODULUS, E' (MPa)
TEMPERATURE (°C)

Figure 4

Large deformation stress-strain measurements were carried out according to procedures described briefly above and in greater detail elsewhere (5). Figure 5 shows several representative results for the PS/1,2B diblocks while Figure 6 presents similar data for PS/PB-1 materials. In all cases, the stress level at a given strain increases as the nature of the solvent used in the preparation becomes more like a good solvent for polystyrene. These observations are in keeping with the general trends seen in the dynamic mechanical tests. In a series of tests conducted at various strain rates on cyclohexane-cast samples, some of the surprising rubbery behavior of these diblock specimens again appears in that they exhibit large deformations without exhibiting the liquid-like flow behavior expected from uncured diblock copolymers with rubbery continuous morphologies (Figures 7 and 8).

This is brought out more clearly in the results of cyclic experiments. In Figure 9a, a schematic cyclic stress-strain curve is shown along with a definition of an area ratio S/W which represents the percentage of energy dissipated in the strain cycle. Figure 9b shows typical results for the two diblock materials under consideration here. As expected, there is considerable hysteresis in these materials, but the significant amount of recoverable energy is a surprising result for rubbery-continuous diblock copolymers. Even more surprising are the values of unrecovered strain; two versions of this paramenter were measured: ε_o is the value of strain obtained immediately upon driving the specimen back to zero stress and ε_{15} is the zero stress value of strain after fifteen minutes of recovery time. Table 5 reveals the trends shown by these paramenters.

Taken overall, the results of the large deformation mechanical experiments are remarkable in that they reveal that these diblock copolymers are capable of undergoing very large extensions and that they can recover their original length nearly completely. There is considerable energy dissipation during stretching,

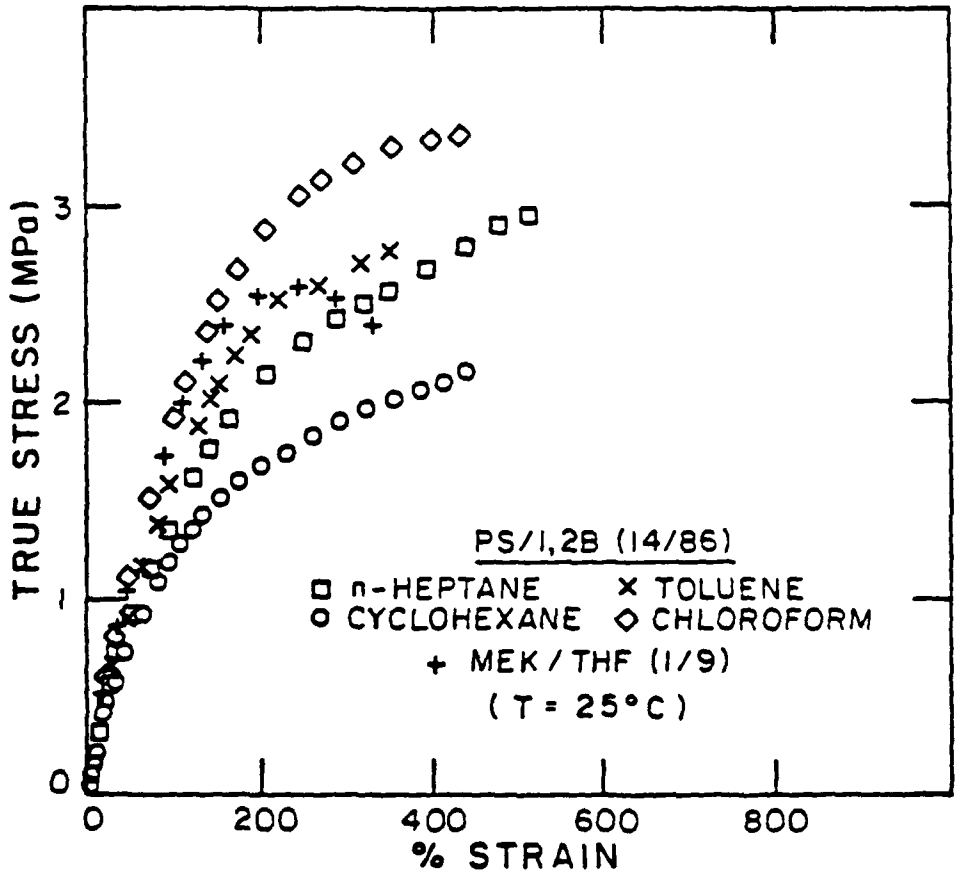

TRUE STRESS (MPa)
0
1
2
3
0
200
400
600
800
% STRAIN
PS/1,2B (14/86)
□ n-HEPTANE
× TOLUENE
○ CYCLOHEXANE
◇ CHLOROFORM
+ MEK / THF (1/9)
(T = 25°C)

Figure 5

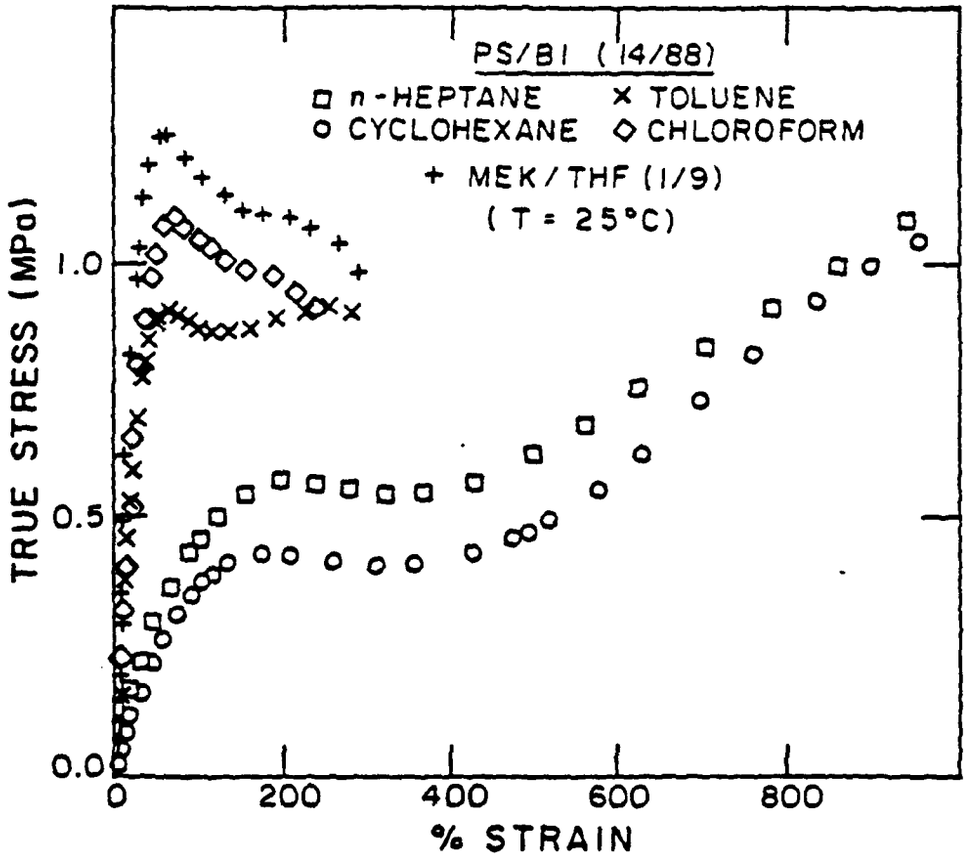

PS/BI (14/88)
□ n-HEPTANE × TOLUENE
○ CYCLOHEXANE ◇ CHLOROFORM
+ MEK/THF (1/9)
(T = 25°C)
TRUE STRESS (MPa)
1.0
0.5
0.0
0
200
400
600
800
% STRAIN

Figure 6

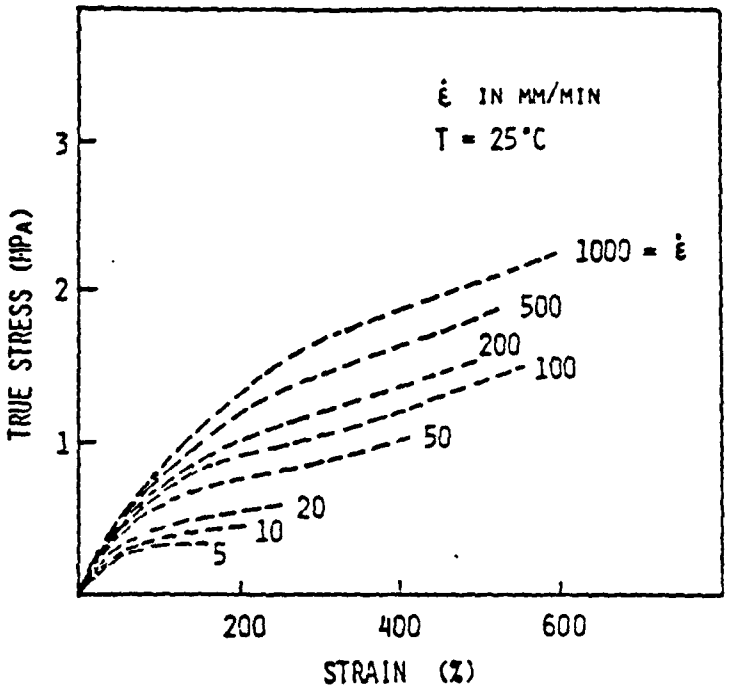


Figure 7

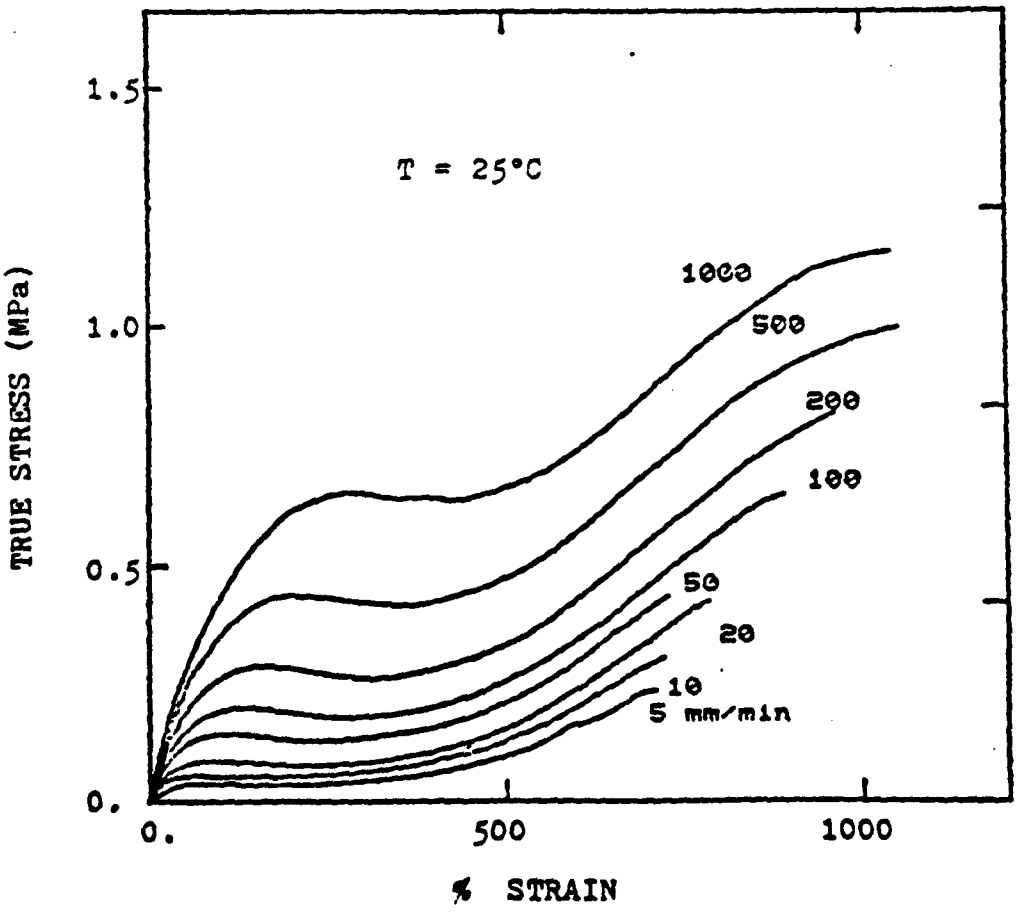


Figure 8

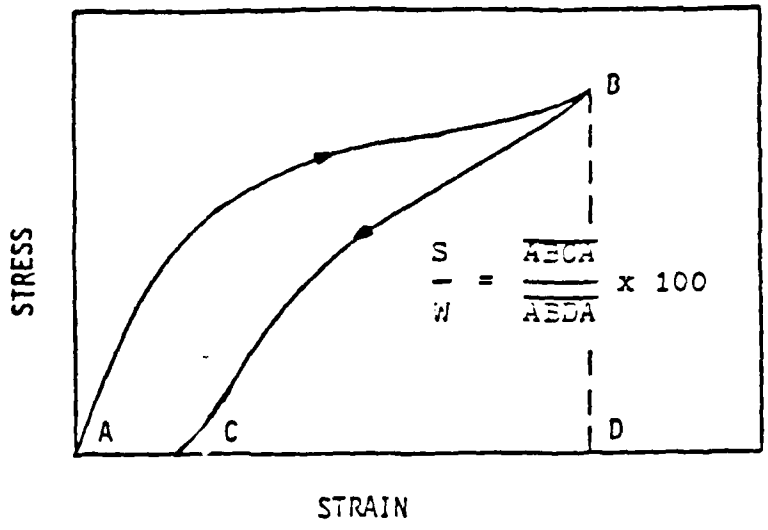


Figure 9a

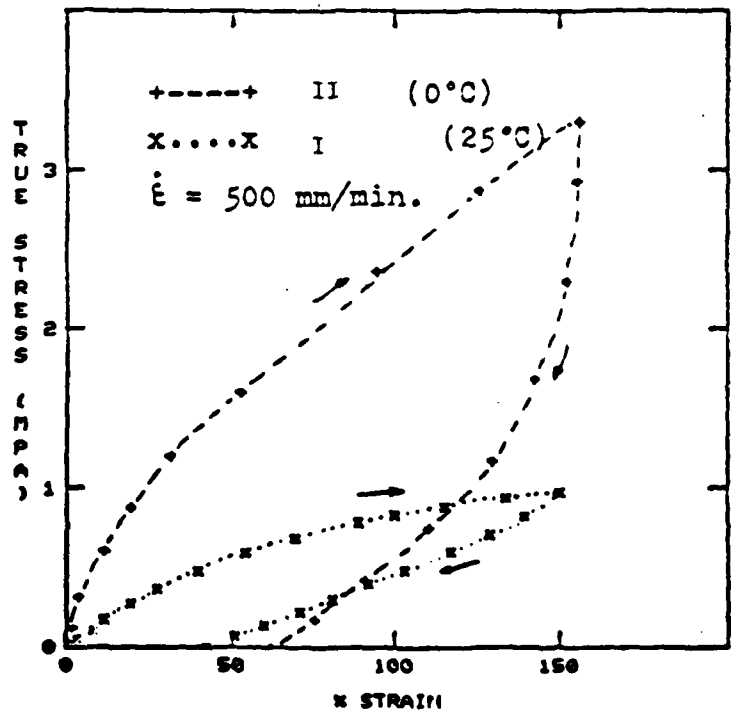


Figure 9b

Table 5 Results of Cyclic Stress-Strain Experiments at 25°C

Sample	Casting Solvent	Maximum Strain of Cyclic Test	Strain Rate of Cyclic test	ε_o	ε_{15}	S/W
I	cyclohexane	150%	500mm/min	15%	1.5%	32%
I'	cyclohexane	150%	500mm/min	42%	6.2%	52%
I	toluene	150%	500mm/min	20%	4.9%	34%
I'	toluene	150%	500mm/min	57%	10%	82%
I	cyclohexane	450%	500mm/min	--	--	66%
I'	cyclohexane	450%	500mm/min	--	--	79%
I	cyclohexane	150%	100mm/min	--	--	46%
II	cyclohexane	150%	100mm/min	--	--	41%

but there is clearly some mechanism which acts to restore the sample nearly to its undeformed length. Purely elastic restoring effects of the rubbery chains, anchored in some way at both ends in glassy domains, would not explain the observed hysteresis. Thus, an explanation at the morphological is more plausible. Evidently there is a weak reticular network of PS-rich material in these samples which is partially disrupted during the stretching process but which reforms relatively rapidly when stress is released. This tendency to reform a particular morphology could provide the driving force for strain recovery to low permanent sets while the break-up of this morphology during the loading cycle provides much of the hysteretic mechanism. Flow in the uncrosslinked rubbery phases of these diblocks occurs only to a surprisingly small extent. The increase in hysteresis and permanent set seen when good solvents for polystyrene are used to form the specimens supports this line of reasoning.

CONCLUSIONS

Although certain effects of hydrogenation could be seen in the results, the one most clearly revealed was a decrease in rubber-phase T_g. The glass-to-rubber transition region was also significantly broadened by the hydrogenation. The overall mechanical response of these materials, both in large and small deformation experiments, appeared to be dominated by the overall morphology more than the molecular level details. The reason for this appears to be that the composition of the materials is just in the region which on the basis of theory is expected to be between the rod-like and sperical microphase forms for the PS domains. Small angle X-ray scattering results were consistent with this conclusion. The results of dynamic mechanical experiments and large deformation stress-strain experiments support the view that a reticular morphology of PS is responsible for the unusual mechanical response of these diblocks, not the particular characteristics of the rubbery chains.

REFERENCES

(1) A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Central Survey," Academic Press, New York, 1977.

(2) A. F. Halasa, D. F. Lohr, and J. E. Hall, J. Polymer Sci, Chem., 19, 1357 (1981).

(3) A. F. Halasa, D. N. Schutz, D. P. Tate, and V. D. Mochel, Adv. Organometallic Chem., 16, 55 (1980).

(4) R. E. Cohen and D. E. Wilfong, Macromolecules, 15, 370 (1982).

(5) J. M. Torradas, Ph. D. Thesis, M. I. T. Department of Chemical Engineering, 1982.

(6) A. F. Halasa, U. S. Patents 3,868,354 (1975); 3,872,072 (1975).

(7) K. L. Hoy, J. Paint Technol, 42, 76 (1970).

(8) J. Brandrup and E. H. Immergut, eds., "Polymer Handbook", 2nd ed., Wiley, New York, 1975.

(9) F. S. Bates, A. S. Argon, and R. E. Cohen, Macromolecules, 16, 1108 (1983).

(10) A. R. Ramos, F. S. Bates, and R. E. Cohen, J. Polymer Sci, Phys., 16, 753 (1968).

(11) E. Helfand and E. R. Wasserman,"Developments in Block Copolymers", I. Goodman, ed., AppliedScience Publishers, Ltd., London, 1982, Chapter 4; Macromolecules 13, 996 (1980); 11, 960 (1978), 9, 897 (1976).

(12) F. S. Bates, C. V. Berney, and R. E. Cohen, Macromolecules, 16, 1101 (1983).

(13) T. Mashimoto, M. Shibayama, and H. Kawai, Macromolecules, 13, 1660 (1980).

(14) R. E. Cohen and F. S. Bates, J. Polymer Sci, Phys., 18, 2143 (1980).

(15) G. Kraus and V. W. Rollman, J. Polymer Sci, Phys., 14, 1133 (1976).

(16) B. Morese-Seguela, M. St. Jaques, J. M. Renaud, and J. Prud'homme, Macromolecules, 13, 100 (1980).

(17) J. Bares, Macromolecules, 8, 244 (1975).

(18) R. E. Cohen and N. W. Tschoegl, Int. J. Polymeric Mater., 2, 49 (1972).

472:GAN:716-4
94/GEN

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

472:GAN:716-4
94/356A-B

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U. S. Department of Commerce Washington, D.C. 20234	2
Naval Surface Weapons Center Attn: Dr. J. M. Augl, Dr. B. Hartman White Oak Silver Spring, Maryland 20910	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Professor Hatsuo Ishida Department of Macromolecular Science Case-Western Reserve University Cleveland, Ohio 44106	1
Dr. David Soong Department of Chemical Engineering University of California Berkeley, California 94720	
Dr. Curtis W. Frank Department of Chemical Engineering Stanford University Stanford, California 94035	
Picatinny Arsenal Attn: A. M. Anzalone, Building 3401 SMUPA-FR-M-D Dover, New Jersey 07801	1
Dr. J. K. Gillham Department of Chemistry Princeton University Princeton, New Jersey 08540	1
Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
NASA-Lewis Research Center Attn: Dr. T. T. Serofini, MS-49-1 2100 Brookpark Road Cleveland, Ohio 44135	1
Dr. Charles H. Sherman Code TD 121 Naval Underwater Systems Center New London, Connecticut 06320	1
Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02191	1
Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	
Dr. R. S. Roe Department of Materials Science and Metallurgical Engineering University of Cincinnatti Cincinnati, Ohio 45221	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1

472:GAN:716-4
94/356A-B

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Dr. Martin Kaufman Code 38506 Naval Weapons Center China Lake, California 93555	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson AFB, Ohio 45433	1
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1
Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1
Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1
Dr. R. S. Porter Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002	1
Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1
Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Professor Brian Newman Department of Mechanics and Materials Science Rutgers, The State University Piscataway, New Jersey 08854	1
Dr. John Lundberg School of Textile Engineering Georgia Institute of Technology Atlanta, Georgia 30332	1


DATE
ILME